

# Power dissipation in a single molecule junction: Tracking energy levels

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Motivated by recent work [Lee et al. *Nature* **489**, 209 (2013)], on asymmetry features of heat dissipation in the electrodes of molecular junctions, we put forward an idea as a result of heat dissipation in the electrodes. Based on tight-binding model and a generalized Green's function formalism, we describe the conditions under which heat dissipation shows symmetry characteristic and does not depend on the bias polarity. We also show the power dissipated in the junction can be used to detect which energy levels of molecule junction play more or less role in the transmission process. We present this idea by studying a simple toy model and Au- $C_{60}$ -Au junction.

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New and powerful ways of energy conversions are a demanding issue which appeals tremendous attentions from wide range of scientists. In this respect, thermoelectric devices are highly desirable since they deal with conversion of temperature to voltage differences or vice versa<sup>1-3</sup>. Study of charge transport in molecules is very active field, with potential applications in molecular electronics<sup>4</sup> and energy-conversion devices<sup>5-18</sup>. The efficiency of thermoelectric depends on a combination of material properties quantified by the thermoelectric figure of merit  $ZT = S^2\sigma T/\kappa$ , where  $S$  is the thermopower or Seebeck coefficient,  $\sigma$  is an electronic conductivity and thermal conductivity  $\kappa$  contains contributions from electrons as well as phonons. A good thermoelectric device needs to have a good electrical conductivity  $\sigma$ , and simultaneously a poor thermal conductivity  $\kappa$ . However, in normal bulk material these two parameters are highly correlated via the well-known Wiedemann-Franz law. Systems that can independently optimize  $S$  and  $\sigma$  are scarce. Mahan and Sofo<sup>19</sup> considered the optimization of the figure of merit as a mathematical problem and found that for a system with discrete electronic density of states like delta-function, the figure of merit diverges in the absence of any phonon contribution to the thermal conductivity<sup>20,21</sup>. Single-molecule hybrid systems, where a single-molecule is sandwiched between metal electrodes, are one such system where can show a discrete density of states at the frontier molecular orbitals (MOs). Understanding and manipulating these hybrid systems could open new pathways for enhancing thermoelectric performance, impossible in bulk semiconductors due to their fundamentally different transport properties.

Two recent experimental<sup>22</sup> and theoretical<sup>23</sup> works reported that heat is not equally dissipated in both electrodes and this asymmetry depends on the bias polarity. The authors used scanning tunnelling probes with integrated nanothermocouples probed heat dissipation in the electrodes of a molecular junction and showed heat

dissipation can be controlled by transmission characteristics. Motivated by these works, we report here a detailed theoretical analysis of the joule heating in current-carrying single-molecule junctions. By combining the tight-binding model and a generalized Green's function formalism, we investigate different conditions of the heat dissipation of molecular junction and its relation with the electron transport. To this end, we first study transmission and heat dissipation properties of a simple two level systems. Using it as a starting point, we describe the conditions under which heat dissipation shows symmetry characteristic and does not depend on the bias polarity. This conclusion further is supported by numerical effective single-particle tight-binding model. As test systems, we consider  $C_{60}$  molecule sandwiched between to metal (Au) electrodes via single and multiple contacts.

The rest of the paper is organized as follows. In Sec. II we present a detailed formalism for finding transmission in a toy model and its heat dissipation characteristics. In Sec. III we present our numerical results for a real Au- $C_{60}$ -Au junction based on tight-binding model. In Sec. IV we summarize our findings and some technical details are presented in the Appendices.

## I. THEORY AND MODEL

We consider the molecule (introduced as a set of energy levels) placed in between two electrodes (left  $L$  and right  $R$ ) and plays a role of channel. The electrodes are behaved as free electron reservoirs with approximately continuous energy spectra. The electronic transport properties of molecular junctions are govern by quantum mechanical laws. One of most important framework for studying theoretical nanoelectronics is a Landauer frameworks<sup>24</sup>. Landauer approach is based on the description of electron transport through elastic scattering model. The thermalized electrons in reservoirs will be scattered when they come into the channel, but their transport are completely coherent between the electrodes. One can interpret the conductance of channel as an elastic scatterer, by the quantum mechanical prob-

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abilities of transmission  $T(E)$ , that corresponds to electrons with energy  $E$ . Because of the importance of transmission function to calculate all transport properties of nanoscale junctions, we will consider this function for our two-level (toy) model in following.

### A. Transmission for two-level (toy) model

Let us consider a two-terminal system with  $L$  and  $R$  electrodes linked by two-level molecular junction model as Fig.1. For this model, the  $(2 \times 2)$  matrix for an inverse Green function defines as

$$G_{l,k}^{-1} = (E - \epsilon_l)\delta_{l,k} - \Sigma_{l,k}^L(E) - \Sigma_{l,k}^R(E) \quad (1)$$

where the elements of  $(2 \times 2)$  self energy matrices define as follows

$$\Sigma_{l,k}^\alpha(E) = \sum_m \tau_{m,l}^{\alpha,*} g^\alpha(E) \tau_{m,k}^\alpha, \quad \alpha = L, R. \quad (2)$$

in which  $\tau_{l,m}^\alpha$  denote the hybridization matrix elements that connect the two-level, up and down, with the electrodes;  $g^\alpha(E)$  is a complex valued surface Green's function of the uncoupled leads, i.e., the left and right semi-infinite leads. The coupling matrix  $\Gamma(E)$  also known as the broadening functions, is related to the self-energies through

$$\Gamma_{l,k}^\alpha(E) = i(\Sigma_{l,k}^\alpha - \Sigma_{l,k}^{\alpha,*}), \quad (3)$$

that from Eq. (2), one can find

$$\Sigma_{l,k}^{\alpha,*} = \frac{g^{\alpha,*}(E)}{g^\alpha(E)} \Sigma_{l,k}^\alpha \quad (4)$$

so the Eq. (3) can be written as

$$\begin{aligned} \Gamma_{l,k}^\alpha(E) &= i \left( 1 - \frac{g^{\alpha,*}(E)}{g^\alpha(E)} \right) \Sigma_{l,k}^\alpha \\ &= 2(\Im g^\alpha(E)) \sum_m \tau_{m,l}^{\alpha,*} \tau_{m,k}^\alpha \end{aligned} \quad (5)$$

the imaginary part of surface Green's functions is related to the contact density of states as

$$\varrho^\alpha(E) = -\frac{1}{\pi} \Im g^\alpha(E) \quad (6)$$

so we obtain

$$\Gamma_{l,k}^\alpha(E) = 2\pi \varrho^\alpha(E) \sum_m \tau_{m,l}^{\alpha,*} \tau_{m,k}^\alpha \quad (7)$$

One can calculate the transmission from the Green's function method, using the relation

$$T(E) = \text{Tr}\{\Gamma^L G \Gamma^R G^\dagger\} \quad (8)$$

by using of relation (7), the above equation converts to

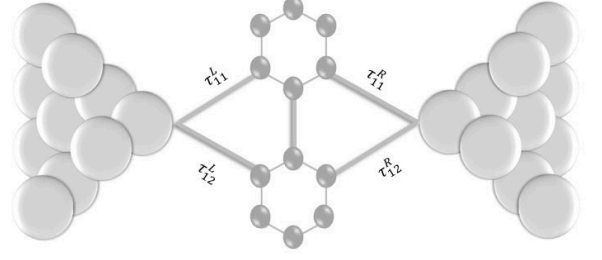


FIG. 1: Schematic representation of the two-level model.

$$T(E) = 4\pi^2 \varrho^L \varrho^R \text{Tr}(\tau^{L,\dagger} \tau^L G \tau^{R,\dagger} \tau^R G^\dagger) \quad (9)$$

since the trace is invariant under cyclic permutations, i.e.,  $\text{Tr}(ABCDEF) = \text{Tr}(BCDEFA)$ , so we can rewrite the above equation as

$$T(E) = 4\pi^2 \varrho^L \varrho^R \text{Tr}(\tau^L G \tau^{R,\dagger} \tau^R G^\dagger \tau^{L,\dagger}) \quad (10)$$

because  $\tau^\alpha = (\tau_{11}^\alpha, \tau_{12}^\alpha)$  is a  $(1 \times 2)$  matrix, so the multiplied  $\tau^L G \tau^{R,\dagger} \tau^R G^\dagger \tau^{L,\dagger}$  is a  $(1 \times 1)$  matrix and equation (10) simplifies as

$$\begin{aligned} T(E) &= 2\pi^2 \varrho^L \varrho^R (\tau^L G \tau^{R,\dagger}) (\tau^R G^\dagger \tau^{L,\dagger})^\dagger \\ &= 2\pi^2 \varrho^L \varrho^R |\tau^L G \tau^{R,\dagger}|^2, \end{aligned} \quad (11)$$

after some calculations and manipulations that are presented in appendices A and B, the above transmission function can be written as

$$T(E) = T_1(E) + T_2(E) + T_{12}(E), \quad (12)$$

where for a system with energies  $\epsilon_i$ s and level broadening  $\gamma_i$ s,  $T_i$ s have a Lorentzian definition

$$T_i(E) = \frac{\gamma_i^2}{(E - \epsilon_i)^2 + \gamma_i^2}, \quad i = 1, 2 \quad (13)$$

and interference enters via

$$T_{12} = (C_1 E + C_2) T_1(E) + (D_1 E + D_2) T_2(E) \quad (14)$$

where constants  $C_i$ s have following definitions

$$C_1 = \frac{2\gamma_2(\epsilon_1 - \epsilon_2)}{\gamma_1[(\epsilon_1 - \epsilon_2)^2 + (\gamma_1 + \gamma_2)^2]} \quad (15)$$

$$C_2 = 2\gamma_2 \frac{\epsilon_1 \epsilon_2 + \gamma_1 \gamma_2 + \gamma_1^2 - \epsilon_1^2}{\gamma_1[(\epsilon_1 - \epsilon_2)^2 + (\gamma_1 + \gamma_2)^2]} \quad (16)$$

and constants  $D_i$ s will obtain by applying  $\epsilon_1 \leftrightarrow \epsilon_2$  and also  $\gamma_1 \leftrightarrow \gamma_2$  exchanges in corresponding  $C_i$ s.

### B. Heat dissipation in two-level model

Let us suppose that a voltage bias  $V$  is applied across the system. It causes that the electrochemical potential of the left and right electrodes shifts such that

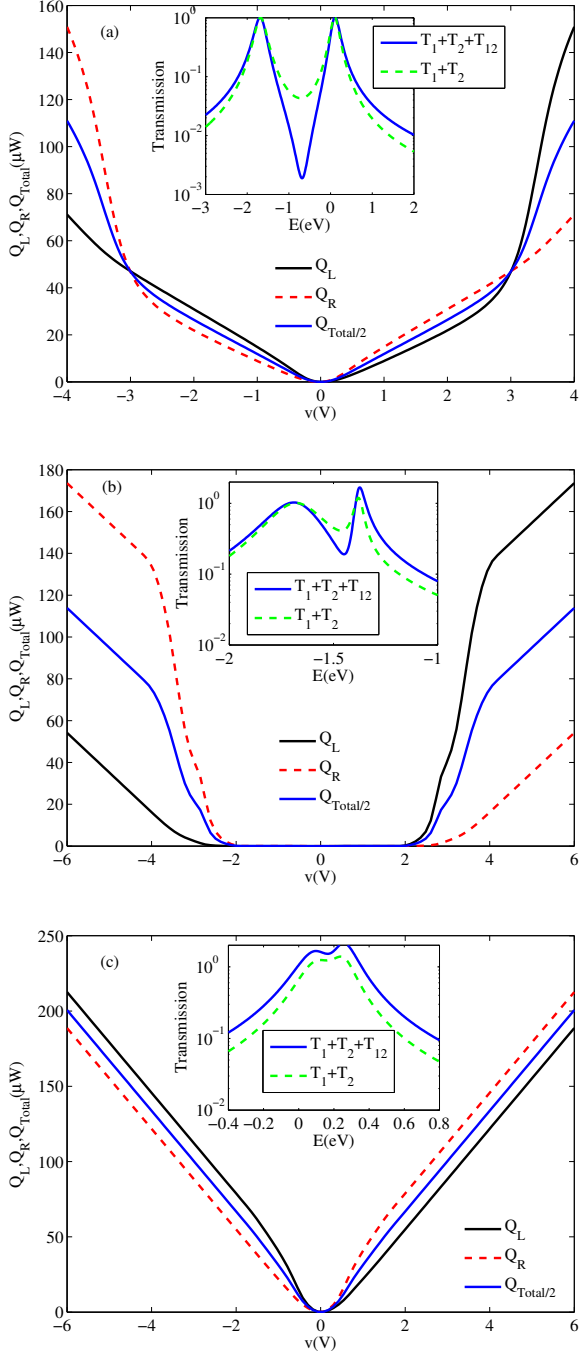


FIG. 2: (Color online) The power dissipated in the left  $Q_L$  electrode (black and solid line), the right  $Q_R$  electrode (red and dashed line) and the total power dissipated  $Q_{Total}$  (blue and solid line) as a function of bias voltage. (a) upper panel for case-1 where energy levels are chosen from HOMO ( $\varepsilon_1 = -1.68$ ) eV and LUMO ( $\varepsilon_2 = 0.1$  eV), (b) middle panel for case-2 which both energies are chosen from HOMOs ( $\varepsilon_1 = -1.68$  eV,  $\varepsilon_2 = -1.38$  eV) and (c) bottom panel for case-3 both where energies are chosen from LUMOs ( $\varepsilon_1 = 0.1$  eV,  $\varepsilon_2 = 0.116$  eV).

$\mu_L - \mu_R = \pm eV$ , where  $e > 0$  is the electron charge. We call positive (negative) bias for plus (minus) sign. On the other words, for positive (negative) bias electrons flow from the left (right) electrode to the right (left) electrode. The fact that elastic scattering is not associated with any energy loss in the junction regions implicitly reminds that when an electron of energy  $E$  tunnels from the left to the right (in positive bias) releases its excess energy  $E - \mu_R$  in the right lead, while the hole, that is created behind the electron, is filled up releasing an energy equal to  $\mu_L - E$  in the left lead. More precisely, these released energies dissipate as a heat in two leads. According to the Landauer approach, the electronic contribution to charge current ( $I$ ) and energy current ( $I_E$ ) through the junction can be expressed in terms of the transmission function for positive bias  $\mu_L - \mu_R = eV$ , as

$$I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} T(E, V) F(E, \mu_L, \mu_R) dE, \quad (17)$$

$$I_E(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} ET(E, V) F(E, \mu_L, \mu_R) dE \quad (18)$$

where  $F(E, \mu_L, \mu_R) = f_L(E, \mu_L) - f_R(E, \mu_R)$  and  $f_{L(R)}(E, V)$  is the Fermi function of the left (right) electrode. Each Fermi function depends on the electrode's chemical potential, which in turn is related to the applied bias. The rate of heat released in the left (right) electrode with electrochemical potential  $\mu_{L(R)}$  is given by

$$Q_{L(R)} = \frac{\mu_{L(R)}}{e} I - I_E, \quad (19)$$

Using Eq. (17) and (18) we obtain the rate of heat dissipated in left and right electrodes as

$$Q_L = \frac{2}{h} \int_{-\infty}^{+\infty} (\mu_L - E) T(E, V) F(E, \mu_L, \mu_R) dE$$

$$Q_R = \frac{2}{h} \int_{-\infty}^{+\infty} (E - \mu_R) T(E, V) F(E, \mu_L, \mu_R) dE \quad (20)$$

thus total power (heat per unit of time) dissipated in the system is

$$Q_{Total}(V) = Q_L(V) + Q_R(V)$$

$$= \frac{2eV}{h} \int_{-\infty}^{+\infty} T(E, V) F(E, \mu_L, \mu_R) dE = IV \quad (21)$$

Three limits allow simplifications of the above relation. First, is the limit that two electrodes to be of the same materials,  $\mu_L = \mu_R = \mu$ , and the system is in equilibrium at zero bias and without loss of generality we set  $\mu = 0$ . Moreover, we assume that the electrochemical potentials are shifted symmetrically with the bias voltage, i.e.  $\mu_L = eV/2$  and  $\mu_R = -eV/2$ . Second, is the limit of zero temperature,  $f_{L(R)}(E, V) \rightarrow \Theta(-E \pm eV)$ , where  $\Theta(x)$  is the Heaviside (step) function. The use of

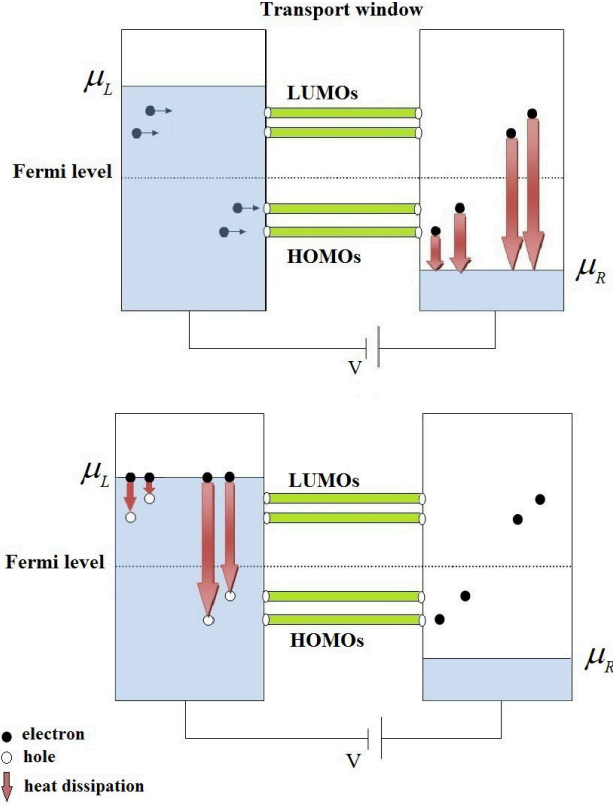


FIG. 3: (Color online) Schematic representation of the power dissipated in a molecular junction. After applying bias voltage transport window opens and molecular orbitals in the window can participate on the transmission processes. Now an electron tunnels from the left electrode to the right electrode, so releases its excess energy  $E - \mu_R$  in the right electrode. For those electron transmitted via the LUMOs orbital more power is dissipated than the HOMOs in the right electrode (see the upper panel). Transmitted electrons leave holes in the left electrode, so the hole is filled up by dissipating an energy equal to  $\mu_L - E$  in the left electrode. For the hole left behind by electron transmitted via the HOMOs orbital more power is dissipated than the LUMOs in the left electrode (see the bottom panel).

plus (minus) signs here arises from the positive (negative) bias. Third, is the low bias limit, where we can neglect the transmission function's dependence on the bias,  $T(E, V) \rightarrow T(E)$ . Applying these limits, we arrive

$$Q_L(V) = \frac{2}{h} \int_{-eV/2}^{+eV/2} (eV/2 - E)T(E)dE, \quad (22)$$

$$Q_R(V) = \frac{2}{h} \int_{-eV/2}^{+eV/2} (E + eV/2)T(E)dE, \quad (23)$$

$$Q_{Total}(V) = \frac{2eV}{h} \int_{-eV/2}^{+eV/2} T(E)dE, \quad (24)$$

If one concentrates on the bias polarity, it is easy to show that

$$Q_{L(R)}(V) = Q_{R(L)}(-V), \quad (25)$$

The above relation indicates that the power dissipated in one of the electrodes can be obtained from the power dissipated in the other one by simply inverting the bias. If one checks the behaviour of total heat dissipation with respect to the inversion of the bias voltage, one obtains

$$\begin{aligned} Q_{Total}(-V) &= Q_L(-V) + Q_R(-V) \\ &= Q_R(V) + Q_L(V) = Q_{Total}(V) \end{aligned} \quad (26)$$

thus, the total heat dissipation is a symmetric function with respect to the inversion of the bias voltage. Also, for total heat we have

$$\begin{aligned} Q_{Total}(V) &= Q_{L(R)}(V) + Q_{R(L)}(V) \\ &= Q_{L(R)}(V) + Q_{L(R)}(-V) \end{aligned} \quad (27)$$

this relation implies that the total power dissipated in the model is equal to the sum of the power dissipated for positive and negative bias in a given electrode. By inserting transmission function (12) in Eq.(24) and taking the integral, we obtain the explicit expression for the total power dissipation in two-level model as

$$\begin{aligned} Q_{Total}(V) &= \frac{2eV\gamma_1}{h} (1 + \varepsilon_1 C_1 + C_2) \left[ \arctan\left(\frac{eV/2 - \varepsilon_1}{\gamma_1}\right) + \arctan\left(\frac{eV/2 + \varepsilon_1}{\gamma_1}\right) \right] + \frac{eV\gamma_1}{h} C_1 \ln \left[ \frac{\gamma_1^2 + (eV/2 - \varepsilon_1)^2}{\gamma_1^2 + (eV/2 + \varepsilon_1)^2} \right] \\ &+ \text{first and second terms with } \{C \leftrightarrow D, \varepsilon_1 \leftrightarrow \varepsilon_2, \gamma_1 \leftrightarrow \gamma_2\} \end{aligned} \quad (28)$$

### C. Numerical results for two-level model

Here, we present our numerical results for the power dissipated of our two-level model between *Au*-electrodes as a function of applied bias. Based on which levels are dominated during the transmission we consider three

cases: case-1: one of the levels is chosen from the highest occupied molecular orbital (HOMO)  $\varepsilon_1 = -1.68eV$  and the other one from the lowest unoccupied molecular orbital (LUMO)  $\varepsilon_2 = 0.1eV$  with  $\gamma_1 = 0.149eV$  and  $\gamma_2 = 0.116eV$ , case-2: both levels are chosen from HOMOs  $\varepsilon_1 = -1.68eV$  and  $\varepsilon_2 = -1.38eV$  below the Fermi energy with  $\gamma_1 = 0.026eV$  and  $\gamma_2 = 0.149eV$  and case-3:

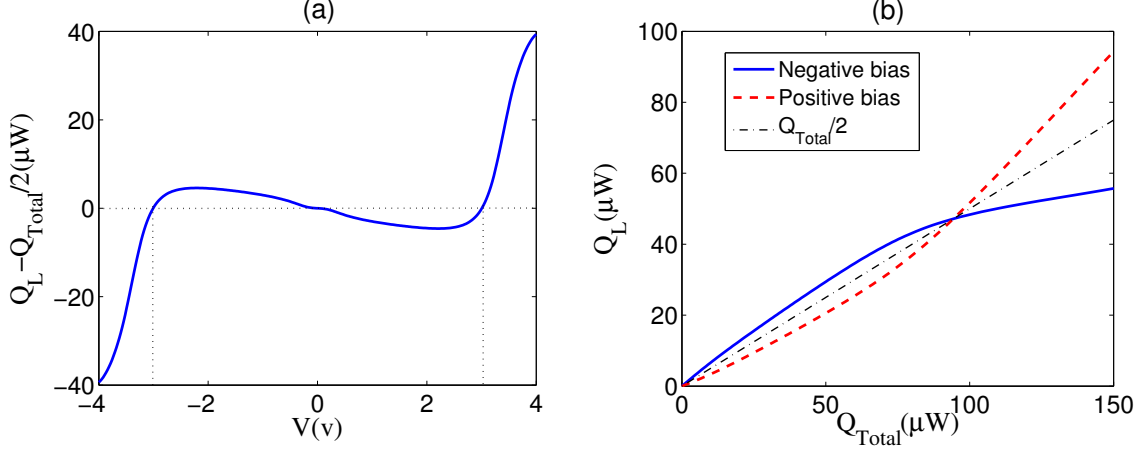


FIG. 4: (Color online) (a) The  $Q_L - Q_{Total}/2$  as a function of the bias. It is indicated that for bias about  $|V_0|=3V$ ,  $Q_L = Q_{Total}/2$ , i.e., symmetric heat dissipated in both electrodes and for  $|V_0| > 3V$  the left electrode has a major portion in total heat dissipation. (b) The power dissipated in the left lead as a function of the total power for positive and negative bias. The dashed line correspond to the power dissipated in a symmetric situation, i.e.  $Q_L(V) = Q_{Total}/2$ . There is an intersection point that in which the heat dissipated in left lead is equal for positive and negative bias and after this point for positive (negative) bias the left electrode has a major (minor) portion in total heat dissipation.

both levels are chosen from LUMOs  $\varepsilon_1 = 0.1eV$  and  $\varepsilon_2 = 0.25eV$  above the Fermi energy with  $\gamma_1 = 0.08eV$  and  $\gamma_2 = 0.116eV$  ( see Fig.2 a-b-c respectively). All the energies are measured with respect to the Fermi energy of the system, which we set to zero ( $E_F = 0$ ). We have borrowed these parameters from table II in ref<sup>27</sup>.

In the all three cases the power dissipation in left and right electrodes is asymmetric and the condition (25) is verified. A detailed elaboration of Fig.2-a shows a cross point between the power dissipated in left and right electrodes  $Q_L(\pm V) = Q_R(\pm V)$  which it does not happen in the other two cases. This cross point means that heat is equally dissipated in both electrodes. From Eq.(22) and Eq.(23) it is easy to show that the condition to have equal heat dissipation in both electrodes is that the transmission function fulfills  $T(-E, -V) = T(E, V)$ . This means the transmission does not depend on the bias voltage and it is also energy independent in the transport window. This is the feature that occurs in any ballistic processes.

Another point we should stress out is that before the crossing point, more (less) heat is dissipated in the right electrode for positive (negative) bias, but after this point two electrodes change their roles and more(less) heat is dissipated in the left electrode for positive (negative) bias (see Fig.2-a). This behavior can be related to the HOMO and LUMO levels domination during the electron transmission processes. Indeed, after turning bias voltage the electrochemical potentials of the left and the right electrodes are shifted and an energy window opens for electrons to cross the junction and it results in a net electron current in the junction. So for the energy-dependent transmission function which is higher in the lower part of the transport window, the more power is dissipated in the left electrode for positive bias (case-2 and see Fig.2-b).

Alternatively, if the transmission is higher in the upper part of the transport window, more heat is dissipated in the right electrode for positive bias (case-3 and see Fig.2-c). A cartoon to present the scenario is depicted in Fig.3

To further investigation of the portion of given electrode, i.e., left electrode, in heat dissipation for our toy model, we plotted the  $Q_L - Q_{Total}/2$  as a function of the bias in Fig.4. Panel (a) of this figure shows that, there is a given positive bias about  $V_0 = 3V$  in which  $Q_L - Q_{Total}/2 = 0$  or  $Q_L = Q_{Total}/2$ , i.e., symmetric heat dissipated in both electrodes. More precise, for positive bias when  $0 < V < V_0$  ( $V > V_0$ ) we find  $Q_L < Q_{Total}/2$  ( $Q_L > Q_{Total}/2$ ) so the portion of left electrode in heat dissipation is less (more) than half of the total heat. This behavior is exactly reversed for negative bias. Briefly, the main conclusion of these results reveals when we plot  $Q_L$  as a function of  $Q_{Total}$  for both positive and negative biases in panel (b). There is a point of intersection that in this point the heat dissipation in left lead is equal for positive and negative bias and after this point for positive (negative) bias the left electrode has a major (minor) portion in total heat dissipation, although before the intersection point, there is no significant difference between the heat dissipation for positive and negative bias.

## II. HEAT DISSIPATION IN THE $C_{60}$ MOLECULE JUNCTIONS

We consider a system consists of a  $C_{60}$  molecule attached to one-dimensional gold ( $Au$ ) electrodes. The whole system is described within a single electron picture

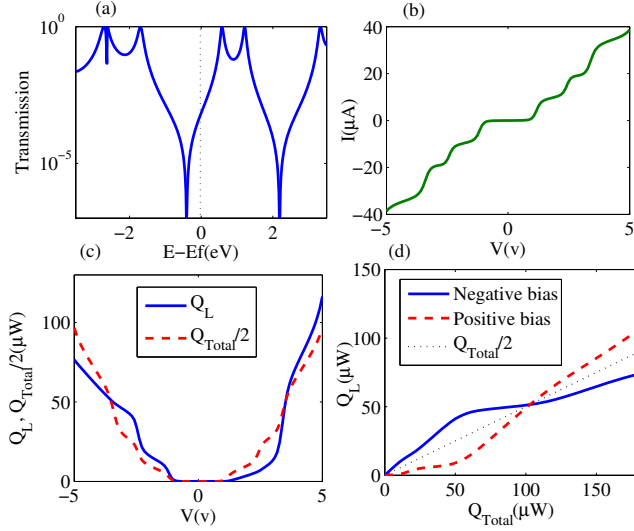


FIG. 5: (Color online) (a) Transmission probability as a function of energy for one contact. (b) Current vs voltage characteristics. (c) Half of the total power dissipated in the junction and the power dissipated in the left lead as a function of the bias. (d) The power dissipated in the left lead as a function of the total power for positive (dashed line) and negative (solid line) bias. The dotted line correspond to the power dissipated in a symmetric situation, i.e.  $Q_L(V) = Q_{Total}/2$ .

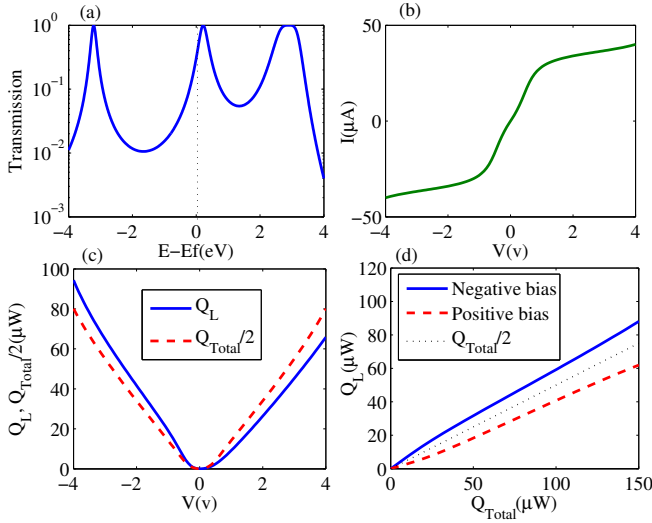


FIG. 6: (Color online) (a) Transmission probability as a function of energy for five-contact. (b) Current vs voltage characteristics. (c) Half of the total power dissipated in the junction and the power dissipated in the left lead as a function of the bias. (d) The power dissipated in the left lead as a function of the total power for positive (dashed line) and negative (solid line) bias. The dotted line correspond to the power dissipated in a symmetric situation, i.e.  $Q_L(V) = Q_{Total}/2$ .

by a tight-binding Hamiltonian with nearest-neighbor hopping approximation. The Hamiltonian representing the entire system can be written as  $H = H_L + V_L + H_M + H_R + V_R$  where  $H_{L/R}$  and  $H_M$  represent the left/right electrode and the  $C_{60}$  molecule, respectively.  $V_{L/R}$  defines the coupling between left/right electrodes and the  $C_{60}$  molecule. In our numerical calculation we used the well-known Newns-Anderson model for gold ( $Au$ ) electrodes, whose self-energies are given by  $\Gamma_{L/R} = V_{L/R} g_{L/R}(E) V_{L/R}^\dagger$ , where  $g_{L/R}(E)$  is the surface Green's function defined as  $g_{L/R}(E) = i \exp(ika/t_{L/R})^{25,26}$ .  $t_{L/R}$  is the nearest-neighboring hopping integral in the left/right electrodes. The hopping strength in  $C_{60}$  molecule depends on the dimerization of the carbon-carbon bonds; thus, we consider different hopping integral elements:  $t_1$  for the single bonds and  $t_2$  for the double bonds. In the numerical calculations we set  $t_1 = 2.5eV^{26}$ ,  $t_2 = 1.1t_1$ ,  $t_{L/R} = t_1$ ,  $E_F = 0.0eV$ , and  $T = 300K$ .

Results for one and five contacts have depicted in Fig.5) and Fig.6), respectively. In Fig.(5-a) we have plotted the logarithmic scale of transmission function versus energy of  $Au-C_{60}-Au$  junctions with one contact. For an electron with energy  $E$ , that comes from the left connection, the probability of transmission function reaches its saturated value (resonance peaks) for the specific energy values. In order to verify heat dissipation feature in the junction, in Fig.(5-d) we present the power dissipated in left lead as a function of the total power dissipated for negative and positive biases. Our results are in good agreement with the simple two-level model. It can be seen that an intersection occurs between the power dissipated in left lead with negative and positive bias. A crossing point in which heat dissipation in leads, finds symmetric features and does not depend on the bias polarity. In Fig.6 we have considered  $C_{60}$  molecule connected to the leads via its pentagon face. The result shows that the transmission function does not display any crossing point between the power dissipated in the left and right electrodes. Therefore, in this case, the power dissipated in the electrodes shows the asymmetry feature in the whole range of applied bias. It shows how heat dissipation in the leads of a two-terminal molecular junction can be specified by its transmission characteristics and from it one can detect which molecular energy levels are more or less dominant in the transmission process.

### III. CONCLUSION

In summary, we have studied heat dissipation in single-molecule junctions. Using the generalized Green's function technique and the Landauer formalism, we have presented a detailed theoretical and numerical analyses of heat dissipation in a simple two level system. We have shown how the transmission characteristics can affect on heat dissipation in the electrodes of a two-terminal junction.



tion. Notably, we have found some points in which asymmetry characteristics of heat dissipation in the left and the right electrodes failed. In other words, at this point heat dissipation is free of bias polarity. To validate our results on the simple toy model, we have chosen C60 molecule sandwiched between Au electrodes. We have simulated a junction based on tight-binding model and Landauer approach. In order to have a different transmission spectrum for an equal energy window we have considered both single and multi contacts cases. The results show how heat dissipation in the leads of a two-terminal molecular junction can be specified by its transmission characteristics and from it one can detect which molecular energy levels are more or less dominant in the transmission process

#### IV. ACKNOWLEDGEMENTS

We are very grateful to Khalil Naimi for his valuable stimulation during this work. We wish you find your health.

##### Appendix A: Transmission for two level model

Suppose a representation with unitary matrix  $U$  which diagonalizes the Green function  $G$  to  $G^d$  as

$$G^d = U^{-1}GU = \begin{pmatrix} \frac{1}{E-z_1} & 0 \\ 0 & \frac{1}{E-z_2} \end{pmatrix} \quad (\text{A1})$$

Thus equation (11) can be written as

$$T(E) = |\eta^L G^d \eta^{R,\dagger}|^2 \quad (\text{A2})$$

This representation will not necessarily diagonalize  $\Gamma^\alpha$  indeed, as will show, interesting quantum interference effects often arise from the non-diagonal elements  $\Gamma^\alpha$ . In this representation, the effective hybridization matrices are

$$\eta^L = \sqrt{2\pi\rho^L}\tau^L U \quad \eta^{R,\dagger} = \sqrt{2\pi\rho^R}U^{-1}\tau^{R,\dagger} \quad (\text{A3})$$

and  $\Gamma^\alpha$  is non-diagonal as

$$U^{-1}\Gamma^\alpha U = \eta^{\alpha,\dagger}\eta^\alpha = \begin{pmatrix} |\eta_{11}^\alpha|^2 & \eta_{11}^{\alpha,*}\eta_{12}^\alpha \\ \eta_{11}^\alpha\eta_{12}^{\alpha,*} & |\eta_{12}^\alpha|^2 \end{pmatrix}, \quad (\text{A4})$$

The expansion of transmission according to effective hybridization matrices elements is

$$T(E) = \left| \frac{\eta_{11}^L\eta_{11}^{R,*}}{E-z_1} + \frac{\eta_{12}^L\eta_{12}^{R,*}}{E-z_2} \right|^2 \quad (\text{A5})$$

the above equation can be expressed with three following terms

$$T(E) = T_1(E) + T_2(E) + T_{12}(E), \quad (\text{A6})$$

the two first terms constitute the non-mixing contributions from each energy level

$$T_1(E) = \frac{|\eta_{11}^L|^2|\eta_{11}^R|^2}{|E-z_1|^2}, \quad T_2(E) = \frac{|\eta_{12}^L|^2|\eta_{12}^R|^2}{|E-z_2|^2} \quad (\text{A7})$$

Interference enters via the third term as

$$T_{12}(E) = 2\Re \left( \frac{\eta_{11}^L\eta_{12}^{L,*}\eta_{11}^{R,*}\eta_{12}^R}{(E-z_1)(E-z_2)^*} \right) \quad (\text{A8})$$

##### Appendix B: Level broadening

According to Eq. (A1) it is straightforward that we have

$$\begin{aligned} \det(G^{-1}) &= \frac{1}{\det(G^d)} = \frac{1}{\det(G)} \\ &= (E-z_1)(E-z_2) \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} \text{Tr}(G^{-1}) &= \frac{1}{\det(G)}\text{Tr}(G) = \frac{1}{\det(G)}\text{Tr}(G^d) \\ &= 2E - (z_1 + z_2), \end{aligned} \quad (\text{B2})$$

The inverse Green function elements of Eq. (1), can be rewritten so that the hermitian and anti-hermitian part of self energy,  $\Sigma = \Sigma^L + \Sigma^R$ , appear in inverse Green function elements as follows

$$\begin{aligned} G_{l,k}^{-1} &= (E - \epsilon_l)\delta_{l,k} - \frac{1}{2}(\Sigma_{l,k}(E) + \Sigma_{l,k}^*(E)) \\ &\quad - \frac{1}{2}(\Sigma_{l,k}(E) - \Sigma_{l,k}^*(E)), \end{aligned} \quad (\text{B3})$$

or

$$G_{l,k}^{-1} = \tilde{G}_{l,k} + \frac{i}{2}\Gamma_{l,k} \quad (\text{B4})$$

in which we have used of

$$\Gamma_{l,k}(E) = i(\Sigma_{l,k}(E) - \Sigma_{l,k}^*(E)), \quad (\text{B5})$$

$$\tilde{G}_{l,k} = (E - \epsilon_l)\delta_{l,k} - \frac{1}{2}(\Sigma_{l,k}(E) + \Sigma_{l,k}^*(E)) \quad (\text{B6})$$

and  $\tilde{G}_{l,k}$  is a hermitian part and last term in (B3) is anti-hermitian part of  $G_{l,k}^{-1}$ . By using of Eqs. (2)-(7) and (A3), above equation will be

$$\begin{aligned} \Gamma_{l,k}(E) &= \sum_{m,n,s} U_{l,m}\eta_{m,n}^{L,\dagger}\eta_{n,s}^L U_{s,k}^{-1} \\ &\quad + \sum_{m,n,s} U_{l,m}\eta_{m,n}^{R,\dagger}\eta_{n,s}^R U_{s,k}^{-1}, \end{aligned} \quad (\text{B7})$$

$$\begin{aligned} \tilde{G}_{l,k} &= (E - \epsilon_l)\delta_{l,k} - \Re g^L(E) \sum_m \tau_{m,l}^{L,*} \tau_{m,k}^L \\ &\quad - \Re g^R(E) \sum_m \tau_{m,l}^{R,*} \tau_{m,k}^R \end{aligned} \quad (\text{B8})$$

It is clear that both  $\tilde{G}$  and  $\Gamma$  are hermitian and so each trace is real and we have

$$\begin{aligned} \text{Tr}(\tilde{G}) &= 2E - (\epsilon_1 + \epsilon_2) - 2\Re g^L(E) (|\tau_{11}^L|^2 + |\tau_{12}^L|^2) \\ &\quad - 2\Re g^R(E) (|\tau_{11}^R|^2 + |\tau_{12}^R|^2) \end{aligned} \quad (\text{B9})$$

$$\text{Tr}(\Gamma) = |\eta_{11}^L|^2 + |\eta_{12}^L|^2 + |\eta_{11}^R|^2 + |\eta_{12}^R|^2, \quad (\text{B10})$$

according to Eq.(B4) we have

$$\text{Tr}(G^{-1}) = \text{Tr}(\tilde{G}) + \frac{i}{2}\text{Tr}(\Gamma), \quad (\text{B11})$$

and by using of Eqs.(B2) and (B9), after the comparison of both sides of above equation, one yields the following conditions

$$\begin{aligned} \Re(z_1 + z_2) &= (\epsilon_1 + \epsilon_2) + 2\Re g^L(E) (|\tau_{11}^L|^2 + |\tau_{12}^L|^2) \\ &\quad + 2\Re g^R(E) (|\tau_{11}^R|^2 + |\tau_{12}^R|^2) \end{aligned} \quad (\text{B12})$$

$$\Im(z_1 + z_2) = \frac{1}{2} (|\eta_{11}^L|^2 + |\eta_{12}^L|^2 + |\eta_{11}^R|^2 + |\eta_{12}^R|^2) \quad (\text{B13})$$

If we consider the following definition for  $z$  quantity

$$z_i = \varepsilon_i + \frac{i}{2}(\gamma_i^L + \gamma_i^R) \quad i = 1, 2 \quad (\text{B14})$$

where  $\varepsilon_i$ s are the energy of the two levels and  $\gamma_i$ s are the broadening by contacts, then according to Eqs. (B12) and (B13) we reach

$$\varepsilon_1 + \varepsilon_2 = (\epsilon_1 + \epsilon_2) + 2\Re g^L(E) (|\tau_{11}^L|^2 + |\tau_{12}^L|^2) + 2\Re g^R(E) (|\tau_{11}^R|^2 + |\tau_{12}^R|^2) \quad (\text{B15})$$

$$\frac{1}{2} (\gamma_1^L + \gamma_1^R + \gamma_2^L + \gamma_2^R) = \frac{1}{2} (|\eta_{11}^L|^2 + |\eta_{12}^L|^2 + |\eta_{11}^R|^2 + |\eta_{12}^R|^2) \quad (\text{B16})$$

the above conditions indicate that the real part of self-energy causes shifts in the system energy levels, while the imaginary part has the effect of level broadening.

In the case of symmetric system-lead coupling, we take  $\gamma_1^L = \gamma_1^R = \gamma_1/2$  and  $\gamma_2^L = \gamma_2^R = \gamma_2/2$ , and effective hybridization matrices elements should satisfy

$$|\eta_{11}^L|^2 = |\eta_{11}^R|^2, \quad |\eta_{12}^L|^2 = |\eta_{12}^R|^2 \quad (\text{B17})$$

so according to Eq. (B13) we obtain

$$\gamma_1 = |\eta_{11}^L|^2 = |\eta_{11}^R|^2, \quad (\text{B18})$$

$$\gamma_2 = |\eta_{12}^L|^2 = |\eta_{12}^R|^2 \quad (\text{B19})$$

In what follows, we suppose that elements of effective hybridization matrices are real, so above relations can be written as

$$\sqrt{\gamma_1} = \eta_{11}^L = \eta_{11}^R, \quad (\text{B20})$$

$$\sqrt{\gamma_2} = \eta_{12}^L = \eta_{12}^R. \quad (\text{B21})$$

and equations (A7) and (A8) have explicit expression as

$$T_i(E) = \frac{\gamma_i^2}{(E - \varepsilon_i)^2 + \gamma_i^2}, \quad i = 1, 2 \quad (\text{B22})$$

$$T_{12}(E) = 2\gamma_1\gamma_2 \frac{(E - \varepsilon_1)(E - \varepsilon_2) + \gamma_1\gamma_2}{((E - \varepsilon_1)^2 + \gamma_1^2)((E - \varepsilon_2)^2 + \gamma_2^2)} \quad (\text{B23})$$

the above relation for  $T_{12}$  can be expanded according to  $T_i$ s as

$$T_{12} = [C_1 E T_1(E) + C_2 T_1(E) + D_1 E T_2(E) + D_2 T_2(E)] \quad (\text{B24})$$

where constants  $C_i$ s have a following definitions

$$C_1 = \frac{2\gamma_2(\varepsilon_1 - \varepsilon_2)}{\gamma_1[(\varepsilon_1 - \varepsilon_2))^2 + (\gamma_1 + \gamma_2)^2]} \quad (\text{B25})$$

$$C_2 = 2\gamma_2 \frac{\varepsilon_1\varepsilon_2 + \gamma_1\gamma_2 + \gamma_1^2 - \varepsilon_1^2}{\gamma_1[(\varepsilon_1 - \varepsilon_2))^2 + (\gamma_1 + \gamma_2)^2]} \quad (\text{B26})$$

and constants  $D_i$ s will obtain by applying  $\varepsilon_1 \leftrightarrow \varepsilon_2$  and also  $\gamma_1 \leftrightarrow \gamma_2$  exchanges in corresponding  $C_i$ s. Finally, we can express transmission function  $T(E)$  as follows

$$T(E) = (1 + C_1 E + C_2)T_1(E) + (1 + D_1 E + D_2)T_2(E), \quad (\text{B27})$$

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